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Organophosphorous Compounds/I V Stalin Metallur-  
gical Institute at Dnepropetrovsk

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1. [ ] a new reaction in organophosphorous compounds developed from previous work of V S Abramov of the S M Kirov Chemical Technological Institute at Kazan. The article is titled "Reaction of Aldehydes with Phosphites", appearing in Doklady Akad Nauk SSSR 95, 991-2 (1954).
2. [ ] this article [ ] significant for the reason that four new organophosphorous compounds are listed, although it is difficult to determine whether any of them are of special interest with regard to biological activity. However, of the four listed, [ ] the first two substances are more apt to be toxic than the other two.
3. [ ] additional Soviet work on organophosphorous compounds in an article titled "Esters of Arylsulfonimidophosphoric Acids" by A V Kirsanov and V I Shevchenko of the I V Stalin Metallurgical Institute at Dnepropetrovsk, appearing in Zhur Obshchei Khim 24, 474-84 (1954). While this work appears to be a routine continuation of Kirsanov's studies of organophosphorous compounds, and [ ] doubt that any of the numerous new compounds listed in the article are of any special interest from the standpoint of biological activity, nevertheless [ ] puzzled as to why the Stalin Metallurgical Institute is interested in this type of work, and why time and effort are being devoted there to research of this nature, as [ ] no apparent connection that these particular substances might bear toward metallurgy.

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4. Because of the possible significance of these two articles, the one by Abramov and the other by Kirsanov and Shevchenko, [ ] translated [ ] as follows:

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$(RO)_3P$  react with aldehydes according to the following scheme:  $(RO)_3P + R'CHO \rightarrow (RO)_3P^+CHR'O^- \rightarrow (RO)_2P(O)CHR'OR$ . The reaction is run in sealed tube with heating several hours at 100-70°, the end of the reaction being detd by disappearance of the phosphite odor. The following were prepd: 22.5%  $(EtO)_2P(O)CH(Et)OEt$ ,  $b_2 115-16^\circ$ ,  $n_D^{20} 1.4340$ ,  $d_{20} 1.036$ ; 23.8%  $(EtO)_2P(O)CHPrOEt$ ,  $b_1 119-20^\circ$ ,  $n_D^{20} 1.4420$ ,  $d_{20} 1.054$ ; 16.7%  $(EtO)_2P(O)CH(OEt)C_6H_4OH-o$ ,  $b_2 174-8^\circ$ ,  $n_D^{20} 1.5075$ ,  $d_{20} 1.180$ ; 15.5%  $(EtO)_2P(O)CH(OEt)C_6H_4Me-p$ ,  $b_1 179-82^\circ$ ,  $n_D^{20} 1.4847$ ,  $d_{20} 1.075$ . The reaction is a new example of reaction of  $(RO)_3P$  with a polar reagent.

To a soln of 0.7 g Na in 15 ml dry MeOH was added with ice-cooling 0.01 mole  $ArSO_2N:PCl_3$  in dry  $C_6H_6$  at below 5°; after filtration and evapn of the filtrate there was obtained a viscous oil, which was shaken with 30 ml  $H_2O$  to dissolve the Na salt of partial esters and to ppt the crystalline  $ArSO_2N=P(OMe)_3$ ; for purification these are taken up in  $C_6H_6$ , washed with  $H_2O$  and evapd after careful drying. The aq exts on acidification with HCl yield 15-20%  $ArSO_2NHPO(OMe)_2$ , from the intermediate  $ArSO_2NNaPO(OMe)_2$ ; the yields of the neutral esters are 70-80%. The trialkyl esters are insol in  $H_2O$ , sol in usual org solvents and can be distd under reduced pressure, but not at atm pressure; they are stable in  $H_2O$  even after heating and are stable to dil mineral acids in the cold, but are slowly hydrolyzed on heating (in one hour refluxing with 0.2N HCl only 5% of a typical ester was hydrolyzed). In aq EtOH the hydrolysis is much more rapid owing to better soly. The hydrolysis yields  $ArSO_2NHPO(OR)_2$ , followed by formation of  $ArSO_2NH_2$  and the isolation of the mono-alkyl esters could not be achieved. The hydrolysis in alkaline media is slower than in acids and yields the Na salts of the di-alkyl esters shown above, and no further reaction takes place. The following  $ArSO_2N=P(OMe)_3$  were obtained (Ar shown): Ph, 75.9%, m 38-40°; o-MeC<sub>6</sub>H<sub>4</sub>, 76%, m 74-5°; p-analog, 80.5%, m 44-5°; 1-C<sub>10</sub>H<sub>7</sub>, 71.7%, m 84-5°; 2-C<sub>10</sub>H<sub>7</sub>, 79.6%, m 93-4°; following  $ArSO_2NHPO(OMe)_2$  were obtained: Ph, 15%, m 108-9°, o-MeC<sub>6</sub>H<sub>4</sub>, 20.4%, m 145-6°; p-analog, 8.95%, m 110-11°; 1-C<sub>10</sub>H<sub>7</sub>, 25%, m 164-5°; 2-C<sub>10</sub>H<sub>7</sub>, 12.3%, m 144-5°. Similarly were run the prepn of the  $ArSO_2N:P(OEt)_3$  but the isolation was changed since colloidal

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NaCl could not be filtered off; the reaction mixtures were concd and treated with a little  $H_2O$  to dissolve the NaCl, after which the products were isolated as above; there were obtained with BuONa in BuOH a similar series of Bu esters. The compounds were:  $ArSO_2N:P(OR)_3$  (Ar, R shown, resp): Ph, Et, liquid, 81.5%; o-MeC<sub>6</sub>H<sub>4</sub>, Et, m 35-7°, 82.1%; p-MeC<sub>6</sub>H<sub>4</sub>, Et, liquid, 78.7%; 1-C<sub>10</sub>H<sub>7</sub>, Et, m 94-5°, 86.4%; 2-C<sub>10</sub>H<sub>7</sub>, Et, m 51-2°, 75.4%;  $ArSO_2NHPO(OR)_2$ : Ph, Et, m 111-12°, 6.82%; o-MeC<sub>6</sub>H<sub>4</sub>, Et, m 97-8°, 9.76%; p-MeC<sub>6</sub>H<sub>4</sub>, Et, m 105-6°, 7.48%; 1-C<sub>10</sub>H<sub>7</sub>, Et, m 154-5°, 8.16%; 2-C<sub>10</sub>H<sub>7</sub>, Et, m 161-2°, 20.4%;  $ArSO_2N:P(OR)_3$ : Ph, Bu, liquid, 85.1%; o-MeC<sub>6</sub>H<sub>4</sub>, Bu, liquid, 88.7%; d<sub>20</sub> 1.111, n<sub>D</sub><sup>20</sup> 1.491; 1-C<sub>10</sub>H<sub>7</sub>, Bu, liquid, 86.9%, d<sub>20</sub> 1.141, n<sub>D</sub><sup>20</sup> 1.530; 2-C<sub>10</sub>H<sub>7</sub>, Bu, liquid, 90.9%, d<sub>20</sub> 1.135, n<sub>D</sub><sup>20</sup> 1.532. Hydrolysis  $ArSO_2N:P(OR)_3$  in alc NaOH one hour at reflux gave the following  $ArSO_2NHPO(OR)_2$ : Ph, Me, 93%, m 108-9°; 1-C<sub>10</sub>H<sub>7</sub>, Me, 95%, m 164-5°; 2-C<sub>10</sub>H<sub>7</sub>, Me, 92%, m 144-5°; o-MeC<sub>6</sub>H<sub>4</sub>, Et, 96.7%, m 97-8°; 1-C<sub>10</sub>H<sub>7</sub>, Et, 96.1%, m 154-5°; 2-C<sub>10</sub>H<sub>7</sub>, Et, m 161-2°, 96.1%; 1-C<sub>10</sub>H<sub>7</sub>, Bu, 92.5%, m 75-7°. To 1.04 g Na dissolved in 30 ml dry ROH was added with stirring at 40-50° 0.01 mole  $ArSO_2N:PCl_3$  in C<sub>6</sub>H<sub>6</sub>, after which the solvents were removed in vacuo, the residue taken up in 20 ml H<sub>2</sub>O and acidified yielding 74-92%  $ArSO_2NHPO(OR)_2$ . Heating 31.03 g 1-C<sub>10</sub>H<sub>7</sub>SO<sub>2</sub>NH<sub>2</sub> with 31.7 g pure PCl<sub>5</sub> in 35 ml CCl<sub>4</sub> on a steam bath one hour gave after diln with 45 ml hot CCl<sub>4</sub> and cooling, 93.5% 1-C<sub>10</sub>H<sub>7</sub>SO<sub>2</sub>N:PCl<sub>3</sub>, m 110-12° to a murky liquid, clear at 117°. In a 3-3.5 hour reaction was similarly prepd 90.1% 2-C<sub>10</sub>H<sub>7</sub>SO<sub>2</sub>N:PCl<sub>3</sub>, m 130-2° (from CCl<sub>4</sub>). Both react rather slowly with H<sub>2</sub>O yielding the sulfonamides; the reaction is more rapid in alkali; the first step of hydrolysis yielding  $ArSO_2NHPOCl_2$  is some seven times faster than the second step in which the amide is formed.

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